CLAIMS

1. A mixed electronic/O^{2-}-anion conductive material of perovskite crystal structure, the electrical neutrality of the crystal lattice of which is preserved characterized in that it consists essentially of a compound of formula (I):

$$A^{(a)}_{(1-x-u)}A'^{(a-1)}_{x}A''^{(a'')}_{u}B^{(b)}_{(1-s-y-v)}B^{(b+1)}_{s}B'^{(b+\beta)}_{y}B''^{(b'')}_{v}O_{3-\delta}, \quad (I)$$

in which formula (I):

a, a-1, a", b, b+1, b+β and b" are integers representing the respective valences of the atoms A, A', A", B, B' and B"; and a, a", b, b", β, x, y, s, u, v and δ are such that the electrical neutrality of the crystal lattice is preserved;

$a > 1$;

a", b and b" are greater than zero;

$-2 \leq \beta \leq 2$;

$a + b = 6$;

$0 < s < x$;

$0 < x \leq 0.5$;

$0 \leq u \leq 0.5$;

$(x + u) \leq 0.5$;

$0 \leq y \leq 0.9$;

$0 \leq v \leq 0.9$;

$0 \leq (y + v + s) \leq 0.9$;

$[u(a'' - a) + v(b'' - b) - x + s + \beta y + 2\delta] = 0$;

and $\delta_{min} < \delta < \delta_{max}$ with

$\delta_{min} = [u(a - a'') + v(b - b'') - \beta y]/2$ and

$\delta_{max} = [u(a - a'') + v(b - b'') - \beta y + x]/2$;

and in which formula (I):

A represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides or alkaline-earth metals;

A', which differs from A, represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides or alkaline-earth metals;

A", which is different from A and A', represents

an atom chosen from aluminum (Al), gallium (Ga), indium (In) and thallium (Tl);

B represents an atom chosen from the transition metals that can exist in several possible valences;

B', which differs from B, represents an atom chosen from transition metals, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn) and lead (Pb); and

B", which differs from B and B', represents an atom chosen from transition metals, metals of the alkaline-earth family, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn) and lead (Pb).

2. The material as defined in claim 1, for which, in formula (I), δ is equal to an optimum value δ_{opt} that allows it to ensure an optimum ionic conductivity for sufficient stability under operating temperature and pressure conditions as a mixed ionic/electronic conductor.

3. The material as defined in either of claims 1 or 2, for which, in formula (I), a and b are equal to 3.

4. The material as defined in one of claims 1 to 3, in which, in formula (I), u is equal to zero.

5. The material as defined in one of claims 1 to 3, in which, in formula (I), u is different from zero.

6. The material as defined in one of claims 1 to 5, for which, in formula (I), the sum (y + v) is equal to zero.

7. The material as defined in one of claims 1 to 5, for which, in formula (I), the sum (y + v) is different from zero.

8. The material as defined in one of claims 1 to 7,

for which, in formula (I), A is chosen from La, Ce, Y, Gd, Mg, Ca, Sr or Ba.

9. the material as defined in claim 8, of formula (Ia):

$$La^{(III)}_{(1-x-u)}A'^{(II)}_{x}A''^{(a'')}_{u}B^{(III)}_{(1-s-y-v)}B^{(IV)}_{s}B'^{(3+\beta)}_{y}B''^{(b'')}_{v}O_{3-\delta} \quad (Ia),$$

corresponding to formula (I) in which a and b are equal to 3 and A represents lanthanum.

10. The material as defined in one of claims 1 to 9, for which, in formula (I), A' is chosen from La, Ce, Y, Gd, Mg, Ca, Sr or Ba.

11. The material as defined in claim 10, of formula (Ib):

$$A^{(III)}_{(1-x-u)}Sr^{(II)}_{x}A''^{(a'')}_{u}B^{(III)}_{(1-s-y-v)}B^{(IV)}_{s}B'^{(3+\beta)}_{y}B''^{(b'')}_{v}O_{3-\delta} \quad (Ib),$$

corresponding to formula (I) in which a and b are equal to 3 and A' represents strontium.

12. The material as defined in one of claims 1 to 11, for which, in formula (I), B is chosen from Fe, Cr, Mn, Co, Ni and Ti.

13. The material as defined in claim 12, of formula (Ic):

$$A^{(III)}_{(1-x-u)}A'^{(II)}_{x}A''^{(a'')}_{u}Fe^{(III)}_{(1-s-y-v)}Fe^{(IV)}_{s}B'^{(3+\beta)}_{y}B''^{(b'')}_{v}O_{3-\delta} \quad (Ic),$$

corresponding to formula (I) in which b = 3 and B represents an iron atom.

14. The material as defined in one of claims 1 to 13, for which, in formula (I), B' is chosen from Co, Ni, Ti and Ga.

15. The material as defined in one of claims 1 to 14, for which, in formula (I), B" is chosen from Ti or Ga.

16. The material as defined in claim 15, of formula (Id),

$$La^{(III)}_{(1-x)}Sr^{(II)}_{x}Fe^{(III)}_{(1-s-v)}Fe^{(IV)}_{s}B''^{(b'')}_{v}O_{3-\delta} \quad (Id),$$

corresponding to formula (I) in which a = b = 3, u = 0, y = 0, B represents an iron atom, A is a lanthanum atom and A' is a strontium atom.

17. The material as defined in one of claims 1 to 16, for which, in formula (I), A" is chosen from Ba, Al and Ga.

18. The material as defined in one of claims 1 to 17, for which formula (I) is either:

$La^{(III)}_{(1-x-u)}\ Sr^{(II)}_{x}\ Al^{(III)}_{u}\ Fe^{(III)}_{(1-s-v)}\ Fe^{(IV)}_{s}\ Ti_{v}\ O_{3-\delta}$,

$La^{(III)}_{(1-x-u)}\ Sr^{(II)}_{x}\ Al^{(III)}_{u}\ Fe^{(III)}_{(1-s-v)}\ Fe^{(IV)}_{s}\ Ga_{v}\ O_{3-\delta}$,

$La^{(III)}_{(1-x)}\ Sr^{(II)}_{x}\ Fe^{(III)}_{(1-s-v)}\ Fe^{(IV)}_{s}\ Ti_{v}\ O_{3-\delta}$,

$La^{(III)}_{(1-x)}\ Sr^{(II)}_{x}\ Fe^{(III)}_{(1-s-v)}\ Fe^{(IV)}_{s}\ Ga_{v}\ O_{3-\delta}$ or

$La^{(III)}_{(1-x)}\ Sr^{(II)}_{x}\ Fe^{(III)}_{(1-s)}\ Fe^{(IV)}_{s}\ O_{3-\delta}$.

19. The material of formula (Id) as defined in claim 16, in which x is equal to 0.4, B" represents a trivalent gallium atom, v is equal to 0.1 and $\delta = 0.2 - (s/2)$ and δ is preferably equal to $\delta_{opt} = 0.180 \pm 0.018$.

20. A method of preparing a mixed electronic/O^{2-} anion conductive material of perovskite crystal structure, the electrical neutrality of the crystal lattice of which is preserved, represented by the crude formula (I'):

$$A_{(1-x-u)}A'_{x}A''_{u}B_{(1-y-v)}B'_{y}B''_{v}O_{3-\delta}, \quad (I')$$

in which formula (I'):

x, y, u, v and δ are such that the electrical neutrality of the crystal lattice is preserved;

$0 < x \leq 0.5$;

$0 \leq u \leq 0.5$;

$(x + u) \leq 0.5$;

$0 \leq y \leq 0.9$;

$0 \leq v \leq 0.9$;

$0 \leq (y + v) \leq 0.9$; and

$0 < \delta$

and in which formula (I'):

A represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides or alkaline-earth metals;

A', which differs from A, represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides or alkaline-earth metals;

A", which is different from A and A', represents an atom chosen from aluminum (Al), gallium 9Ga), indium (In) and thallium (Tl);

B represents an atom chosen from the transition metals that can exist in several possible valences;

B', which differs from B, represents an atom chosen from transition metals, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn) and lead (Pb); and

B", which differs from B and B', represents an atom chosen from transition metals, metals of the alkaline-earth family, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn) and lead (Pb);

characterized in that it comprises the following successive steps:

- a step (a) of synthesizing a powder having an essentially perovskite crystal phase from a blend of compounds consisting of at least one carbonate and/or of an oxide and/or of a sulfate and/or of a nitrate and/or of a salt of each of the elements A, A' and B and, if necessary, of a carbonate and/or of an oxide of A", B' and/or B";

- a step (b) of forming the powder blend obtained from step (a);

- a step (c) of removing the binder from the formed material obtained from step (b); and

- a step (d) of sintering the material obtained from step (c);

and characterized in that at least one of steps (a), (c) and (d) is carried out while controlling the oxygen

partial pressure (pO_2) of the gaseous atmosphere surrounding the reaction mixture.

21. The method as defined in claim 20, characterized in that step (c) is carried out while controlling the oxygen partial pressure (pO_2) of the gaseous atmosphere surrounding the material from which the binder is to be removed.

22. The method as defined in claim 20 or 21, in which step (d) is carried out in a gaseous atmosphere having an oxygen partial pressure not exceeding 0.1 Pa.

23. The method as defined in claim 22, in which step (a) is carried out in air.

24. A mixed electronic/O^{2-} anion conductive material of perovskite crystal structure, the electrical neutrality of the crystal lattice of which is preserved, represented by the crude formula (I'):

$$A_{(1-x-u)}A'_xA''_uB_{(1-y-v)}B'_yB''_vO_{3-\delta}, \qquad (I')$$

in which formula (I'):

x, y, u, v and δ are such that the electrical neutrality of the crystal lattice is preserved;

$0 < x \leq 0.5$;

$0 \leq u \leq 0.5$;

$(x + u) \leq 0.5$;

$0 \leq y \leq 0.9$;

$0 \leq v \leq 0.9$;

$0 \leq (y + v) \leq 0.9$; and

$0 < \delta$

and in which formula (I'):

A represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides or alkaline-earth metals;

A', which differs from A, represents an atom chosen from scandium, yttrium or from the families of lanthanides, actinides or alkaline-earth metals;

A", which is different from A and A', represents

an atom chosen from aluminum (Al), gallium (Ga), indium (In) and thallium (Tl);

B represents an atom chosen from the transition metals that can exist in several possible valences;

B', which differs from B, represents an atom chosen from transition metals, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn) and lead (Pb); and

B", which differs from B and B', represents an atom chosen from transition metals, metals of the alkaline-earth family, aluminum (Al), indium (In), gallium (Ga), germanium (Ge), antimony (Sb), bismuth (Bi), tin (Sn) and lead (Pb);

and in which δ depends on the oxygen partial pressure in the gaseous atmospheres in which steps (a), (d) and optionally (c) of the method as defined in one of claims 20 to 23 take place.

25. Use of the material as defined in one of claims 1 to 19 and 24 as mixed conductive material of a catalytic membrane reactor designed to be used to synthesize syngas by the oxidation of methane or natural gas.

26. Use of the material as defined in one of claims 1 to 19 and 24 as mixed conductive material of a ceramic membrane designed to be used to separate oxygen from air.